

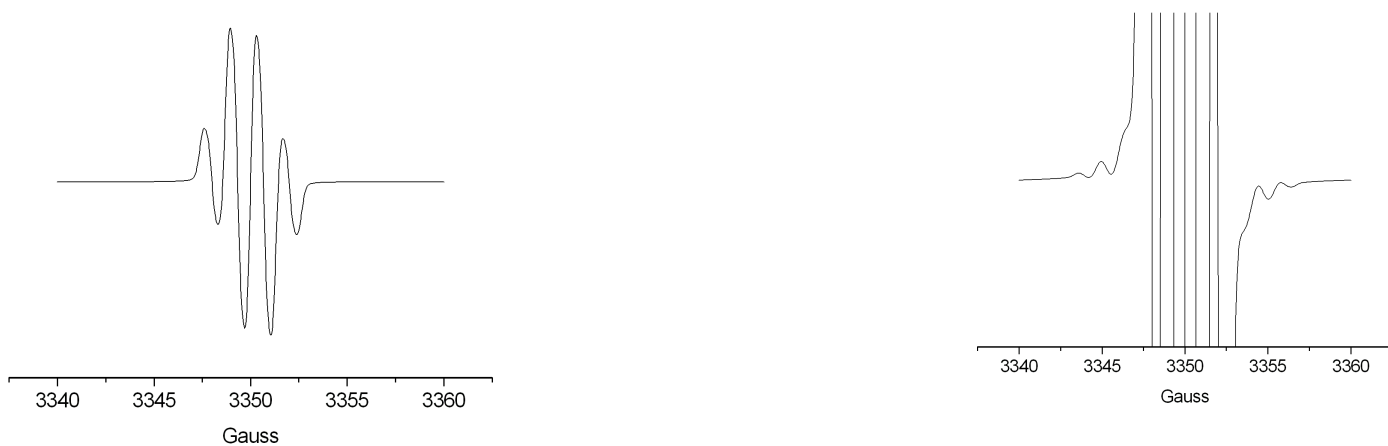
Supplementary Material (ESI) for PCCP  
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## **Bis(Tetrathiafulvalenes) with Aromatic Bridges: Electron Delocalization in the Oxidized Species through EPR and Theoretical Studies**

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### **Supplementary Material**

**Fig. S1. EPR spectrum simulated for (Pyr-TTF)<sup>•+</sup> by using the coupling constants obtained from DFT calculations.**

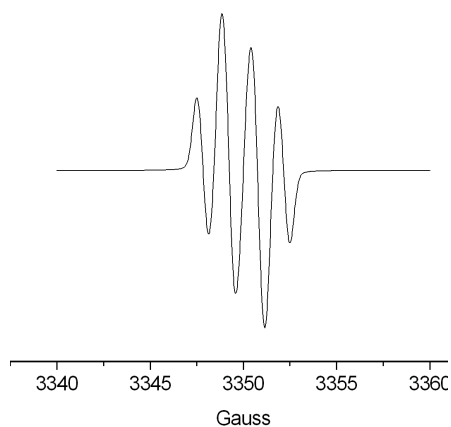


**spectrum a**

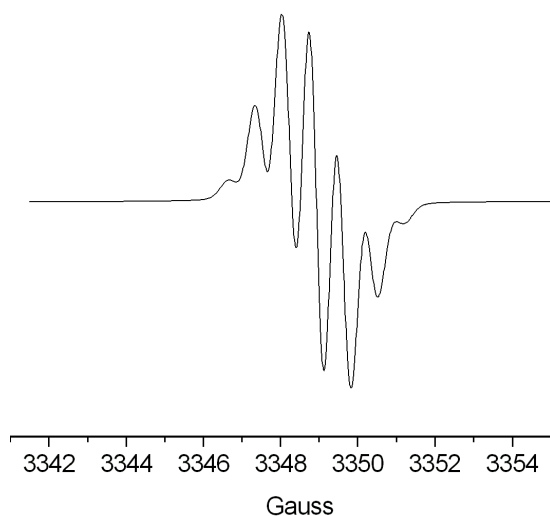
**spectrum b**

spectrum **b** has been simulated with an expansion of the y-scale in order to show the satellite lines due to <sup>33</sup>S.

**Fig. S2. EPR spectrum simulated for (Bz-TTF)<sup>•+</sup> by using the coupling constants obtained from DFT calculations**



**Fig. S3.** EPR spectrum simulated for  $(\text{TTF-Pyr-TTF})^{\cdot+}$  by using the coupling constants obtained from DFT calculations



**Fig. S4.** Experimental EPR spectra obtained after oxidation of  $(\text{TTF-Bz-TTF})_{\text{meta}}$ .

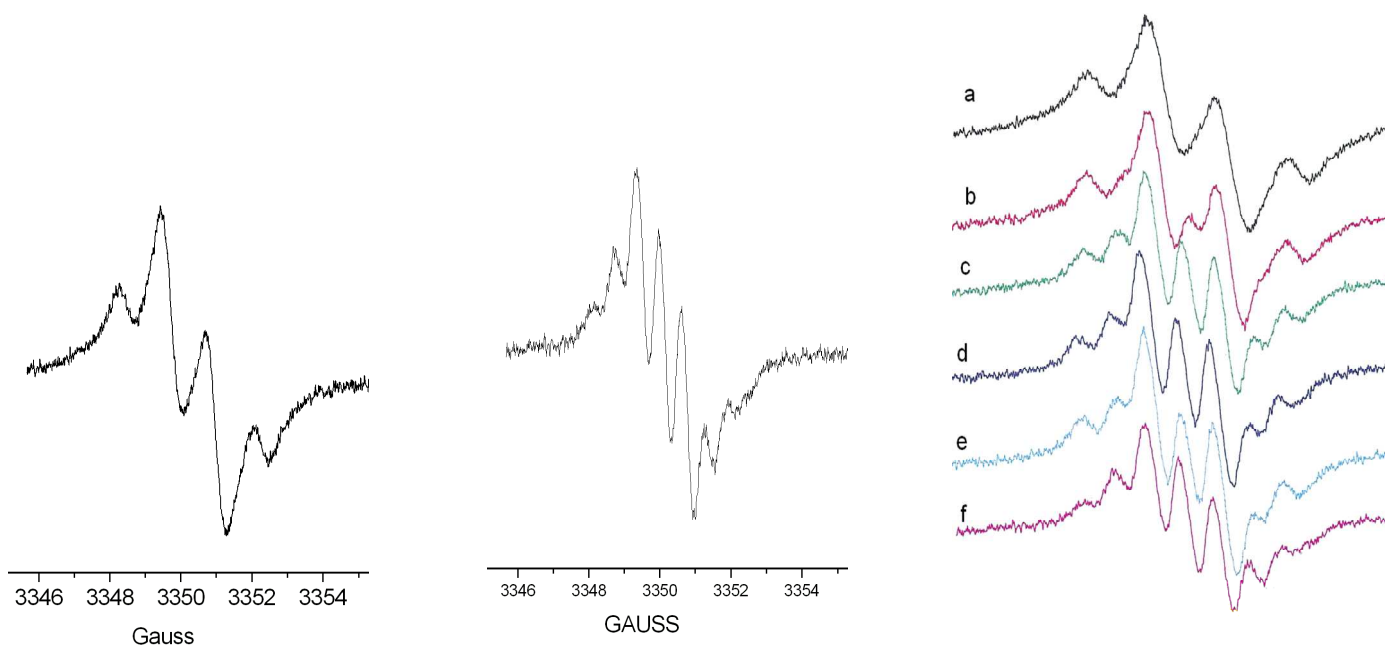


Fig. S4a.

Fig. S4b

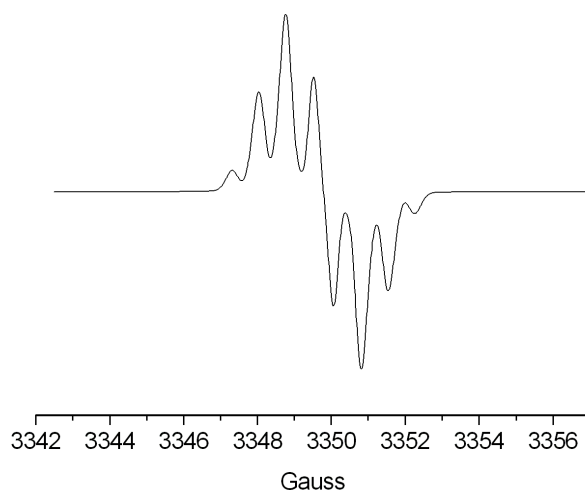
Fig. S4c

**Fig. S4a:** Oxidation of  $\text{TTF-Bz-TTF}$  with 20 equivalents of ferricinium  $\text{PF}_6$

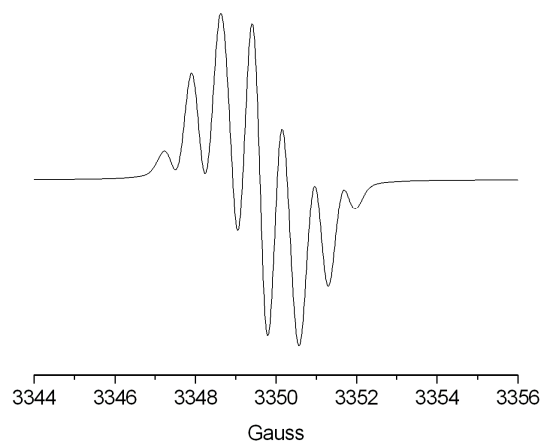
**Fig. S4b:** Oxidation of  $\text{TTF-Bz-TTF}$  with 0.01 equivalents of ferricinium  $\text{PF}_6$

**Fig. S4c:** variation of the hyperfine pattern with the amount of ferricinium  $\text{PF}_6$  (in equivalents). a: 20 equiv., b: 2 equiv., c: 1.5 equiv., d: 1 equiv., e: 0.5 equiv., f: 0.1 equiv.

**Fig. S5.** EPR spectrum simulated for  $(\text{TTF-Bz-TTF})_{\text{meta}}^{\cdot+}$  by using the coupling constants obtained from DFT calculations.

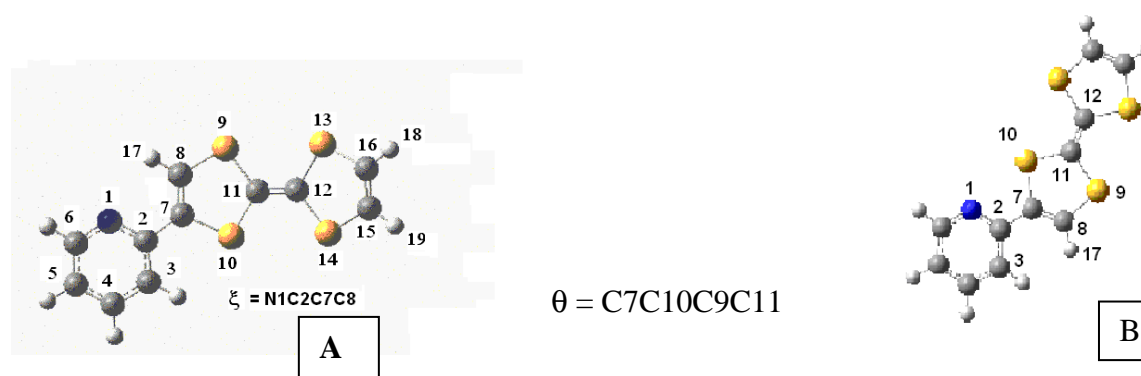


**Fig. S6.** EPR spectrum simulated for  $(\text{TTF-Bz-TTF})_{\text{para}}^{\cdot+}$ .



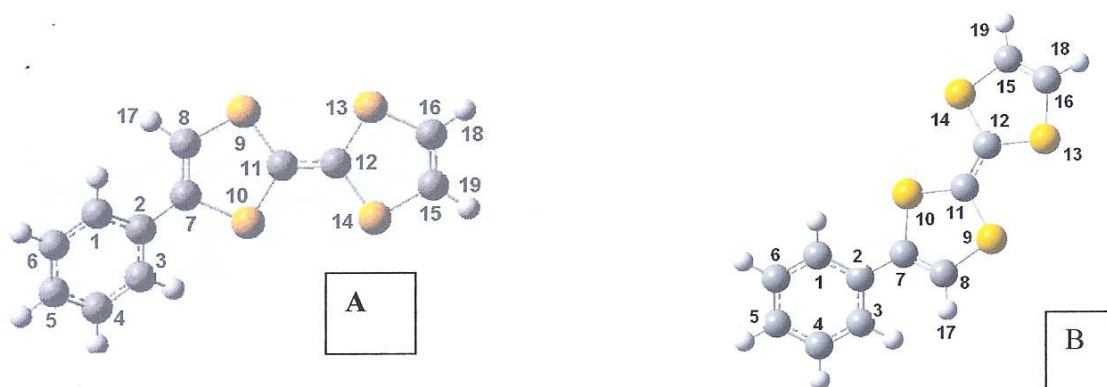
Simulation was performed by using the following coupling constants: -0.90 G (with two protons), -0.65G ( with two protons), -0.63 (with two protons).  
The DFT coupling constants are very slightly different: -1.51 (for H17, H17'), -0.64 (for H18, H18'), -0.59 (for H19,H19'), for H1, H1', H3, H3' coupling are less than 0.09G).

**Table S1a.** Solvent and conformation dependences of the  $^1\text{H}$  and  $^{14}\text{N}$  coupling constants ( $\text{Pyr-TTF})^+$



	H17	H18	H19	H-C3	H-C4	H-C5	H-C6	N1
<b>(Pyr-TTF)<sup>+</sup></b> <b>conformation A</b> $\xi = 0^\circ, \theta = 180^\circ$								
No solvent	-1.626	-1.212	-1.237	-0.394	0.130	-0.465	0.163	0.188
THF	-1.412	-1.309	-1.338	-0.355	0.122	-0.450	0.115	0.120
$\text{CH}_2\text{Cl}_2$	-1.390	-1.313	-1.342	-0.355	0.121	-0.443	0.115	0.120
$\text{H}_2\text{O}$	-1.628	-1.337	-1.364	-0.348	0.115	-0.405	0.115	0.117
<b>conformation B</b> $\xi = 180^\circ, \theta = 180^\circ$								
No solvent	-1.578	-1.263	-1.263	-0.098	0.003	-0.281	-0.211	-0.141
THF	-1.273	-1.345	-1.351	-0.199	0.011	-0.276	-0.076	-0.046
$\text{CH}_2\text{Cl}_2$	-1.249	-1.347	-1.355	-0.198	0.008	-0.274	-0.071	-0.043
$\text{H}_2\text{O}$	-1.126	-1.356	-1.377	-0.194	0.003	-0.266	-0.05	-0.030

**Table S1b. Solvent and conformation dependences of the  $^1\text{H}$  coupling constants for  $(\text{Bz-TTF})^+$**

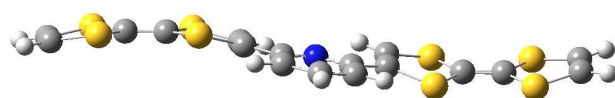
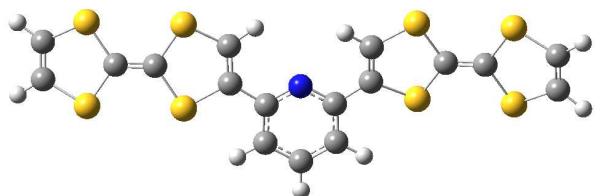


$$\xi = \text{C1C2C7C8}, \theta = \text{C7C10C9C11}$$

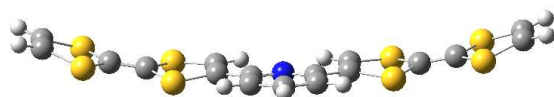
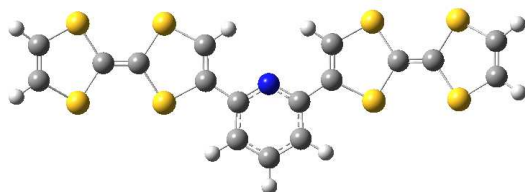
	H17	H18	H19	H-C3	H-C4	H-C5	H-C6	H-C1
<b><math>(\text{Bz-TTF})^+</math></b> conformation A $\xi = -33.1^\circ, \theta = -177.5^\circ$								
No solvent	-2.003	-1.227	-1.233	-0.106	0.130	-0.338	0.061	-0.140
THF	-1.726	-1.306	-1.296	-0.124	0.124	-0.315	0.134	-0.200
$\text{CH}_2\text{Cl}_2$	-1.712	-1.308	-1.298	-0.130	0.128	-0.310	0.133	-0.200
$\text{H}_2\text{O}$	-1.623	-1.312	-1.310	-0.155	0.135	-0.319	0.126	-0.206
<b>conformation B</b> $\xi = 146.5^\circ, \theta = -177.5^\circ$								
No solvent	-2.003	-1.227	-1.233	-0.140	0.061	-0.338	0.130	-0.106
THF	-1.726	-1.306	-1.296	-0.200	0.134	-0.315	0.124	-0.124
$\text{CH}_2\text{Cl}_2$	-1.712	-1.308	-1.298	-0.200	0.133	-0.310	0.128	-0.130
$\text{H}_2\text{O}$	-1.623	-1.312	-1.310	-0.206	0.126	-0.319	0.135	-0.155

**Table S2. Equilibrium conformations calculated for neutral TTF-Pyr-TTF**

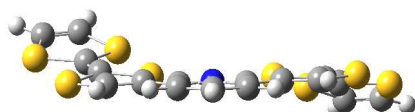
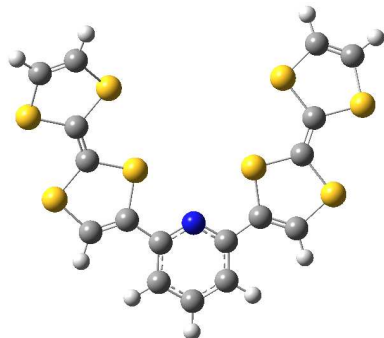
**Min 1 C2 AA (C2 sym)** E= -3893.38347 h,  $\xi_1 = +7.8^\circ$   $\theta_1 = +165.6^\circ$ ,  $\xi_2 = +7.8^\circ$   $\theta_2 = +165.6^\circ$



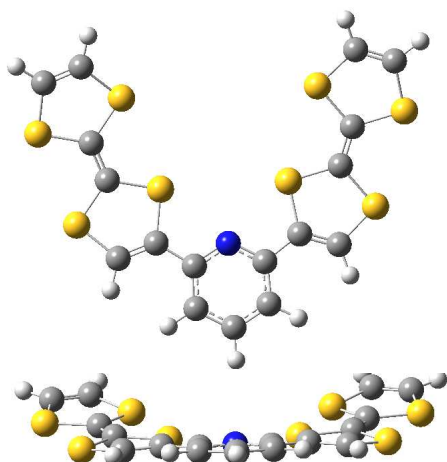
**Min 1 C2 CS AA (Cs sym)** E= -3893.38341 h,  $\xi_1 = -4.04^\circ$   $\theta_1 = -165.9^\circ$ ,  $\xi_2 = +4.04^\circ$   $\theta_2 = 165.9^\circ$



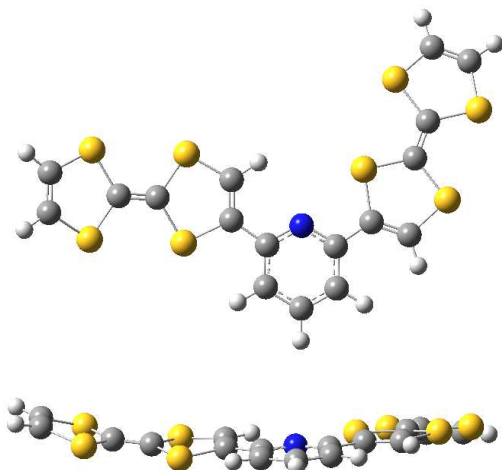
**Min 2 C2 BB (C2 sym)** E= -3893.38394 h,  $\xi_1 = 176.8^\circ$   $\theta_1 = 169.3^\circ$ ,  $\xi_2 = 176.8^\circ$   $\theta_2 = 169.3^\circ$



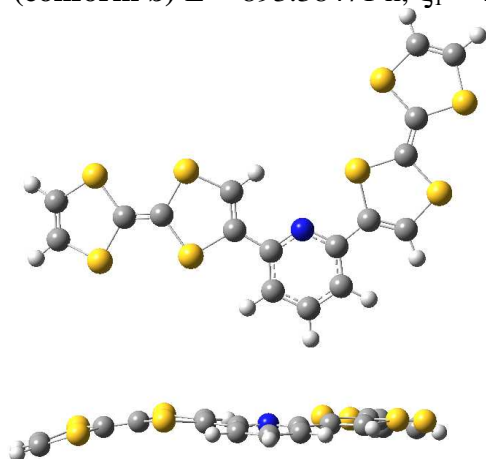
**Min 2 Cs BB(Cs sym)**  $E = -893.38391$  h,  $\xi_1 = 176.1^\circ$   $\theta_1 = 168.8^\circ$ ,  $\xi_2 = -176.1^\circ$   $\theta_2 = -168.8^\circ$



**Min 3 C1a AB (conform a)**  $E = -893.38467$  h  $\xi_1 = -3.4^\circ$ ,  $\theta_1 = 166.6^\circ$ ,  $\xi_2 = 177.7^\circ$ ,  $\theta_2 = 170.8^\circ$



**Min 3 C1b AB (conform b)**  $E = -893.38471$  h,  $\xi_1 = 4.6^\circ$   $\theta_1 = 166.1^\circ$   $\xi_2 = 178.1^\circ$   $\theta_2 = 169.7^\circ$

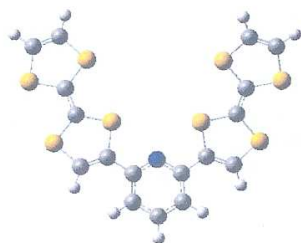




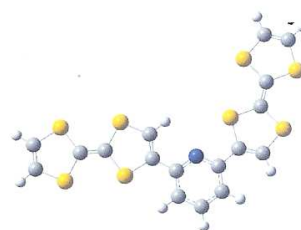
**Table S3. Conformation dependence of the isotropic coupling constants<sup>a</sup> in (TTF-Pyr-TTF)<sup>+</sup>** (the calculations take the solvent effects (THF) into account)



**AA**



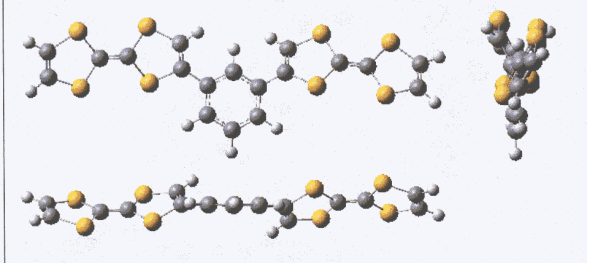
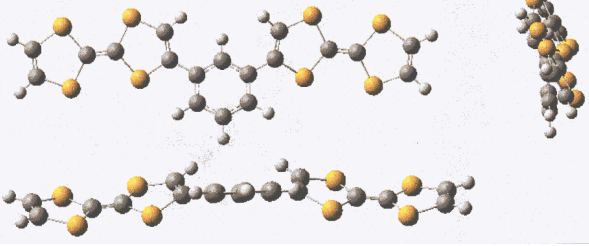
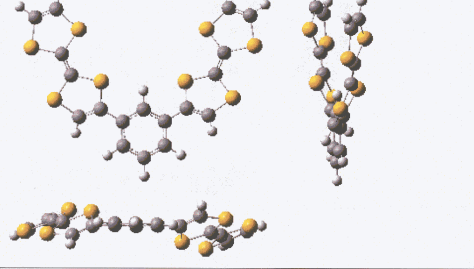
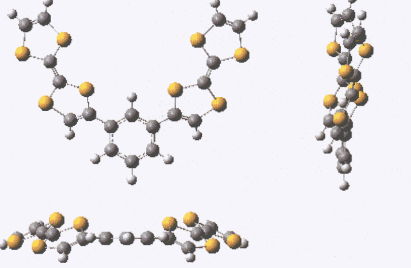
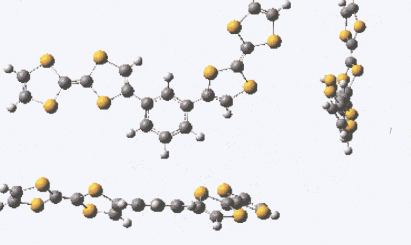
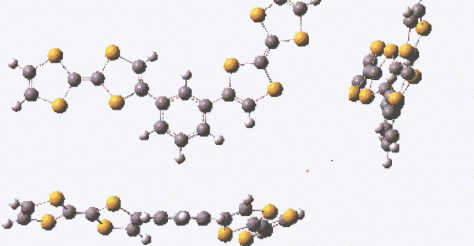
**BB**



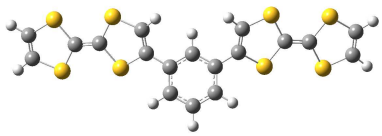
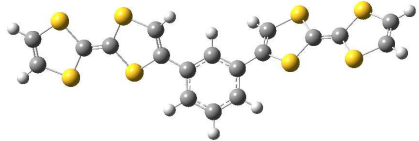
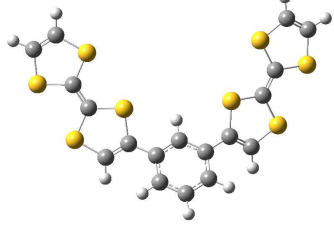
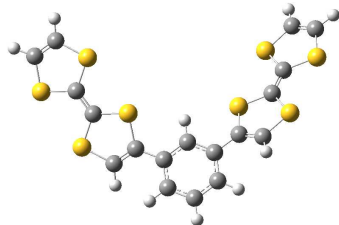
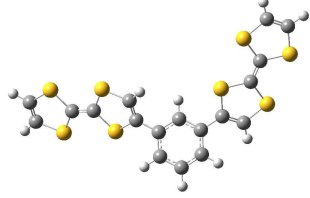
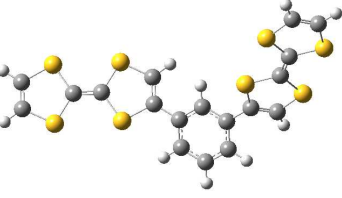
**AB**

	H17	H18	H19	H17'	H18'	H19'	H-C3	H-C3'	H-C4	N1
(TTF-Pyr-TTF) <sup>+</sup>										
Conformation AA $\xi_1 = 0^\circ, \theta_1 = 180^\circ$ $\xi_2 = 0^\circ, \theta_2 = 180^\circ$ E = -3893.17543 a.u. ( $\Delta E = 3.5 \text{ kcal. mol}^{-1}$ )	-0.74	-0.67	-0.69	-0.73	-0.67	-0.69	0.0	0.0	0.10	0.28
Conformation BB $\xi_1 = 180^\circ, \theta_1 = 180^\circ$ $\xi_2 = 180^\circ, \theta_2 = 180^\circ$ E = -3893.18107 a.u. ( $\Delta E = 0.0 \text{ kcal. mol}^{-1}$ )	-1.0	-0.66	-0.63	-1.0	-0.66	-0.63	-0.62	-0.62	0.25	-0.22
Conformation AB $\xi_1 = 0^\circ, \theta_1 = 180^\circ$ $\xi_2 = 180^\circ, \theta_2 = 180^\circ$ E = -3893.17806 a.u. ( $\Delta E = 1.89 \text{ kcal. mol}^{-1}$ )	-0.13	-0.53	-0.56	-0.79	-0.89	-0.85	0.15	-0.02	0.13	0.21
Conformation BA $\xi_1 = 180^\circ, \theta_1 = 180^\circ$ $\xi_2 = 0^\circ, \theta_2 = 180^\circ$	-0.79	-0.89	-0.85	-0.13	-0.53	-0.56	0.13	-0.02	0.15	0.21

**Table S4. Conformations of neutral (TTF-Bz-TTF)<sub>meta</sub>**

<p><b>AA sym C2 (min1)</b></p> <p><b>E = -3877.34014 h    <math>\Delta E=0.08</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= -32.8^\circ</math>            <math>\theta_1=-164.2^\circ</math>  <math>\xi_2= -32.8^\circ</math>            <math>\theta_2= -164.2^\circ</math></p>	
<p><b>AA sym Cs (min1)</b></p> <p><b>E = -3877.33998 h    <math>\Delta E=0.18</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= -33.3^\circ</math>            <math>\theta_1= -164.3^\circ</math>  <math>\xi_2= +33.3^\circ</math>            <math>\theta_2= +164.3^\circ</math></p>	
<p><b>BB sym C2 (min2)</b></p> <p><b>E = -3877.33972 h    <math>\Delta E= 0.35</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= 148.4^\circ</math>            <math>\theta_1= -163.8^\circ</math>  <math>\xi_2= 148.4^\circ</math>            <math>\theta_2=-163.8^\circ</math></p>	
<p><b>AA sym Cs (min2)</b></p> <p><b>E = -3877.33982 h    <math>\Delta E= 0.28</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= 148.1^\circ</math>            <math>\theta_1= -164.0^\circ</math>  <math>\xi_2= -148.1^\circ</math>            <math>\theta_2= +164.0^\circ</math></p>	
<p><b>AB sym C1 (min3, a)</b></p> <p><b>E = -3877.34021 h    <math>\Delta E= 0.04</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= +34.4^\circ</math>            <math>\theta_1=+164.0^\circ</math>  <math>\xi_2= -148.9^\circ</math>            <math>\theta_2=+163.9^\circ</math></p>	
<p><b>AB sym C2 (min3,b)</b></p> <p><b>E = -3877.34027 h    <math>\Delta E= 0.0</math> kcal.mol<sup>-1</sup></b></p> <p><math>\xi_1= -31.37^\circ</math>            <math>\theta_1=-164.0^\circ</math>  <math>\xi_2= -148.6^\circ</math>            <math>\theta_2=+163.3^\circ</math></p>	

**Table S5. Optimized conformations for (TTF-Bz-TTF)<sup>+</sup>**

<p><b>AA</b></p> <p><b>Min1 Cs</b> E=-3877.13219 a.u. (<math>\Delta E = 0.55</math> kcal. mol<sup>-1</sup>)</p> <p><b>Min1 C2</b> E=-3877.13250 a.u. (<math>\Delta E = 0.36</math> kcal. mol<sup>-1</sup>)</p>	 <p><b>Min1 Cs</b> <math>\xi_1 = -33.4^\circ</math>, <math>\theta_1 = -176.7^\circ</math> <math>\xi_2 = 33.4^\circ</math>, <math>\theta_2 = 176.7^\circ</math></p>	 <p><b>Min1 C2</b> <math>\xi_1 = -33.5^\circ</math>, <math>\theta_1 = -176.7^\circ</math> <math>\xi_2 = -33.5^\circ</math>, <math>\theta_2 = -176.7^\circ</math></p>
<p><b>BB</b></p> <p><b>Min2 Cs</b> E=-3877.13307 a.u. (<math>\Delta E = 0</math> kcal. mol<sup>-1</sup>)</p> <p><b>Min2 C2</b> E=-3877.13292 a.u. (<math>\Delta E = 0.09</math> kcal. mol<sup>-1</sup>)</p>	 <p><b>Min2 Cs</b> <math>\xi_1 = 148.7^\circ</math>, <math>\theta_1 = -176.9^\circ</math> <math>\xi_2 = -148.7^\circ</math>, <math>\theta_2 = 176.9^\circ</math></p>	 <p><b>Min2 C2</b> <math>\xi_1 = 148.8^\circ</math>, <math>\theta_1 = -176.9^\circ</math> <math>\xi_2 = 148.8^\circ</math>, <math>\theta_2 = -176.9^\circ</math></p>
<p><b>AB</b></p> <p><b>Min3 C1</b> E=-3877.13272 a.u. (<math>\Delta E = 0.22</math> kcal. mol<sup>-1</sup>)</p> <p><b>Min3 asym</b> E=-3877.13253a.u (<math>\Delta E = 0.34</math> kcal. mol<sup>-1</sup>)</p>	 <p><b>Min3 C1</b> <math>\xi_1 = -39.5^\circ</math>, <math>\theta_1 = -177.0^\circ</math> <math>\xi_2 = -148.1^\circ</math>, <math>\theta_2 = 176.3^\circ</math></p>	 <p><b>Min3 asym</b> <math>\xi_1 = 34.39^\circ</math>, <math>\theta_1 = 177.5^\circ</math> <math>\xi_2 = -141.6^\circ</math>, <math>\theta_2 = 176.8^\circ</math></p>

**Table S6. Isotropic coupling constants<sup>a</sup> for the various conformations of (TTF-Bz-TTF)<sup>+</sup><sub>meta</sub>**

(TTF-Bz-TTF) <sup>+</sup>	H17	H18	H19	H17'	H18'	H19'	H-C3	H-C3'	H-C4	H-C1
<b>Min1 (Cs) AA</b> $\xi_1 = -33.4^\circ, \theta_1 = -176.7^\circ$ $\xi_2 = 33.4^\circ, \theta_2 = 176.7^\circ$	-0.82	-0.68	-0.68	-0.79	-0.68	-0.68	-0.28	-0.02	-0.03	0.19
<b>Min1 pseudo C2 AA</b> $\xi_1 = -33.5^\circ, \theta_1 = -176.7^\circ$ $\xi_2 = -33.5^\circ, \theta_2 = -176.7^\circ$	-0.81	-0.68	-0.67	-0.80	-0.68	-0.67	-0.54	0.19	0.19	-0.05
<b>Min 2 pseudo Cs BB</b> $\xi_1 = 148.7^\circ, \theta_1 = -176.9^\circ$ $\xi_2 = -148.7^\circ, \theta_2 = 176.9^\circ$	-0.74	-0.70	-0.69	-0.76	-0.69	-0.68	-0.34	-0.03	-0.03	0.11
<b>Min2 (C2) BB</b> $\xi_1 = 148.8^\circ, \theta_1 = -176.9^\circ$ $\xi_2 = 148.8^\circ, \theta_2 = -176.9^\circ$	-0.77	-0.70	-0.68	-0.77	-0.70	-0.68	-0.38	0.08	0.08	0.05
<b>Min3 C1 (AB)</b> $\xi_1 = -39.5^\circ, \theta_1 = -177.0^\circ$ $\xi_2 = -148.1^\circ, \theta_2 = 176.3^\circ$	-0.81	-0.89	-0.89	-0.61	-0.49	-0.48	-0.35	0.07	0.0	0.15
<b>Min3 C1 (BA)</b> $\xi_1 = \quad, \theta_1 = \quad$ $\xi_2 = \quad, \theta_2 = \quad$	-0.61	-0.49	-0.48	-0.81	-0.89	-0.89	-0.35	0.0	0.07	0.15
<b>Min3 asym AB</b> $\xi_1 = 34.39^\circ, \theta_1 = 177.5^\circ$ $\xi_2 = -141.6^\circ, \theta_2 = 176.8^\circ$	-0.79	-0.71	-0.71	-0.84	-0.65	-0.64	-0.24	-0.02	-0.06	0.08
<b>Min3 asym BA</b> $\xi_1 = 141.6^\circ, \theta_1 = 176.8^\circ$ $\xi_2 = 34.3^\circ, \theta_2 = 177.6^\circ$	-0.84	-0.65	-0.64	-0.79	-0.71	-0.71	-0.24	-0.06	-0.02	0.08

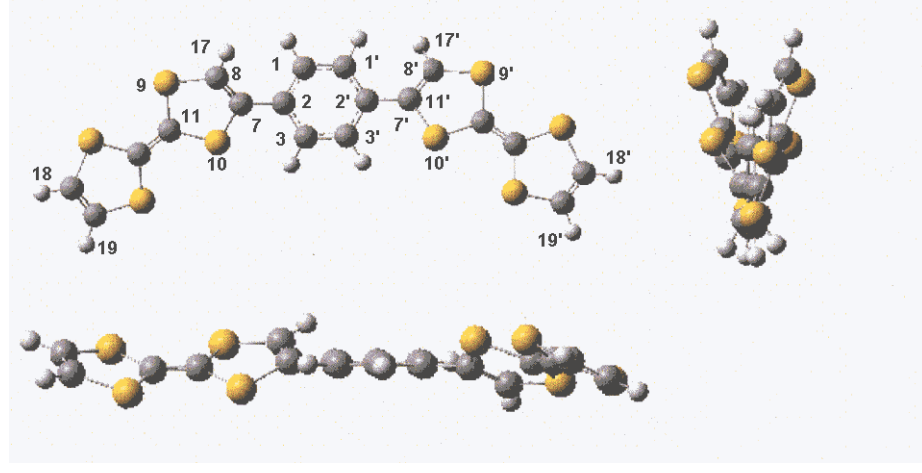
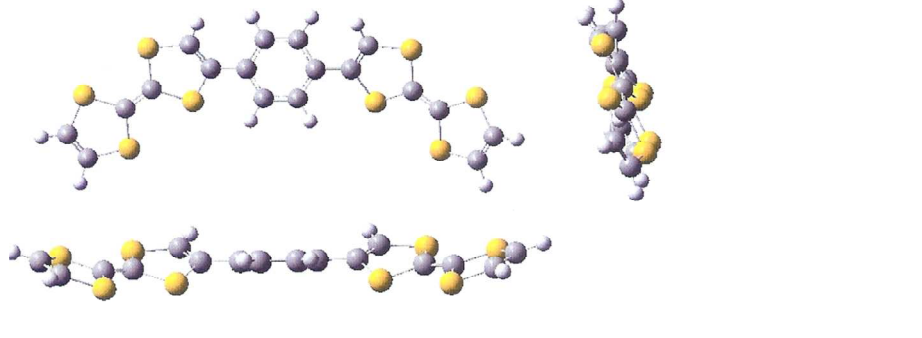
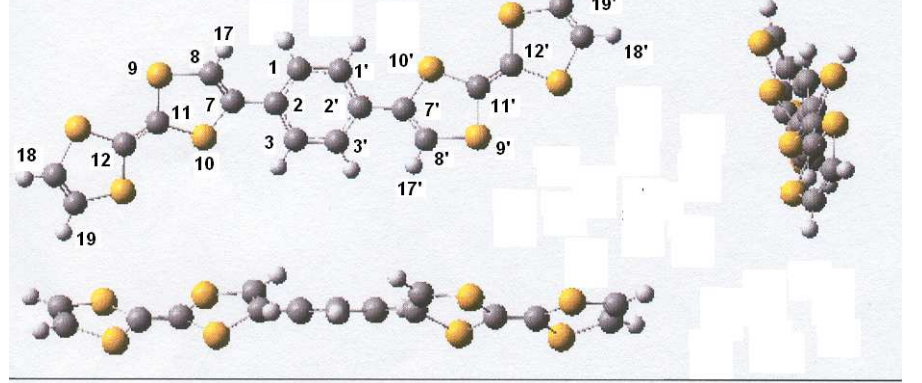
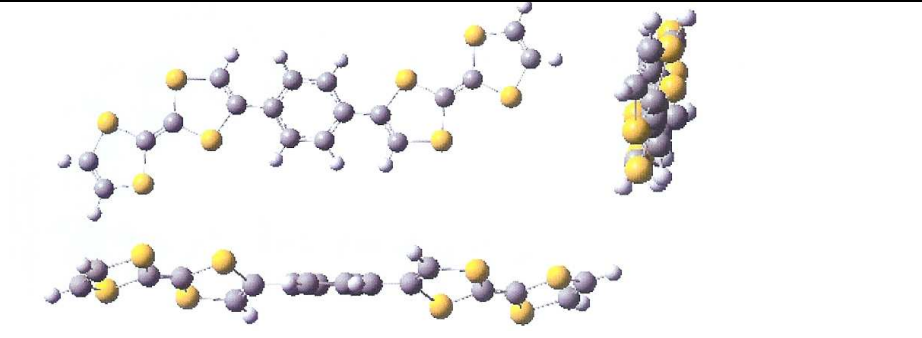
**Table S7. Spin-spin exchange parameters calculated for (TTF-Bz-TTF)<sup>2+</sup><sub>meta</sub>**

	Isomer AA				Isomer BB				Isomer AB	
	J <sub>N</sub> (cm <sup>-1</sup> )		J <sub>Y</sub> (cm <sup>-1</sup> )		J <sub>N</sub> (cm <sup>-1</sup> )		J <sub>Y</sub> (cm <sup>-1</sup> )		J <sub>N</sub> (cm <sup>-1</sup> )	J <sub>Y</sub> (cm <sup>-1</sup> )
<b>BP</b>	C2	Cs	C2	Cs	C2	Cs	C2	Cs	C1	C1
TZV	1.4	0.8	1.2	0.8	0.6	0.0	0.6	0.0	1.5	1.5
Aug-cc-pVDZ	1.2	0.7	1.4	0.7	0.8	-0.1	0.8	-0.1	1.3	1.3
IGLO-III	1.2	0.8	1.2	0.8	0.8	0.0	0.8	0.0	1.3	1.3
<b>B3lyp</b>	C2		C2							
TZV	1.2		1.2							
Aug-cc-pVDZ	1.1		1.1							
IGLO-III	1.1		1.1							

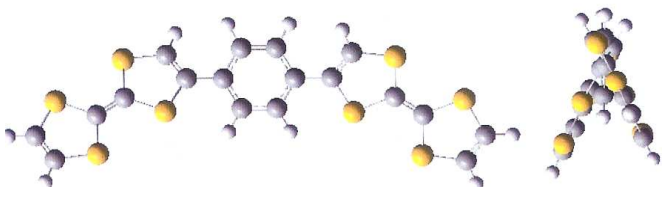
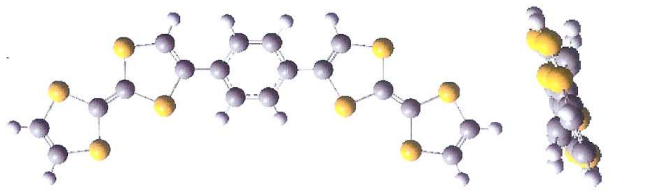
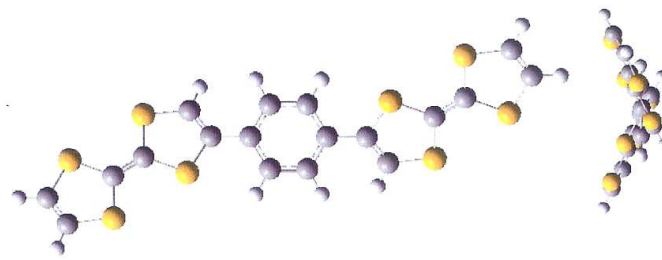
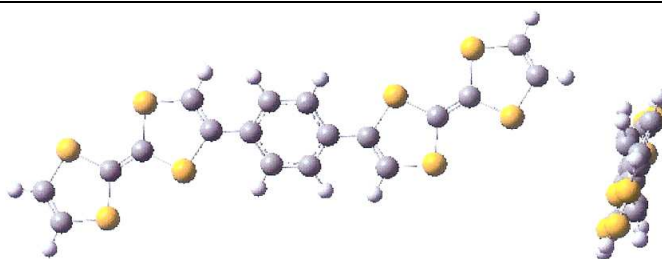
<sup>a</sup> values calculated at the geometry optimized with Gaussian G03 using B3lyp/6-31G

**Table S8. Optimized structures for neutral (TTF-Bz-TTF)<sub>para</sub>**

$\xi_1 = \text{C1C2C7C8}$ ,  $\theta_1 = \text{C7C10C9C11}$ ,  $\xi_2 = \text{C1'C2'C7'C8'}$ ,  $\theta_2 = \text{C7'C10'C9'C11'}$

<p>Rotamer AA (C2)</p> <p>E = -3877.34089 h</p> <p><math>\xi_1 = -28.8^\circ</math></p> <p><math>\theta_1 = -163.5^\circ</math></p> <p><math>\xi_2 = -28.8^\circ</math></p> <p><math>\theta_2 = 163.5^\circ</math></p>	
<p>Rotamer AA (Cs)</p> <p>E = -3877.34096 h</p> <p><math>\xi_1 = 29.6^\circ</math></p> <p><math>\theta_1 = 163.7^\circ</math></p> <p><math>\xi_2 = -29.6^\circ</math></p> <p><math>\theta_2 = -163.7^\circ</math></p>	
<p>Rotamer AB (C2)</p> <p>E = -3877.34085 h</p> <p><math>\xi_1 = -29.8^\circ</math></p> <p><math>\theta_1 = -163.6^\circ</math></p> <p><math>\xi_2 = 150.4^\circ</math></p> <p><math>\theta_2 = -163.5^\circ</math></p>	
<p>Rotamer AB (Ci)</p> <p>E = -3877.34103h</p> <p><math>\xi_1 = 29.7^\circ</math></p> <p><math>\theta_1 = 163.8^\circ</math></p> <p><math>\xi_2 = 149.8^\circ</math></p> <p><math>\theta_2 = -163.8^\circ</math></p>	

**Table S9. Conformations for (TTF-Bz-TTF)<sup>+</sup><sub>para</sub>**

<p>E = -3877.34085 h Min1 C2</p> <p><math>\xi_1 = -28.4^\circ</math>  <math>\theta_1 = -175.6^\circ</math>  <math>\xi_2 = -28.2^\circ</math>  <math>\theta_2 = -175.6^\circ</math></p>	
<p>E = -3877.34085 h Min1 Cs</p> <p><math>\xi_1 = 28.8^\circ</math>  <math>\theta_1 = -175.5^\circ</math>  <math>\xi_2 = -28.5^\circ</math>  <math>\theta_2 = -175.5^\circ</math></p>	
<p>E = -3877.13528 h Min2 C2</p> <p><math>\xi_1 = -28.4^\circ</math>  <math>\theta_1 = -175.7^\circ</math>  <math>\xi_2 = 151.3^\circ</math>  <math>\theta_2 = -175.7^\circ</math></p>	
<p>E = -3877.13543 h Min2 Ci</p> <p><math>\xi_1 = -27.9^\circ</math>  <math>\theta_1 = -175.6^\circ</math>  <math>\xi_2 = -151.8^\circ</math>  <math>\theta_2 = 175.6^\circ</math></p>	

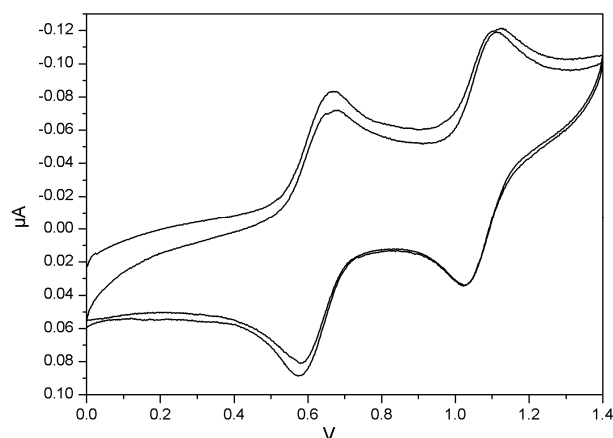
Same atom numbering as in Table sup.7.

$\xi_1 = \text{C1C2C7C8}$ ,  $\theta_1 = \text{C7C10C9C11}$ ,  $\xi_2 = \text{C1'C2'C7'C8'}$ ,  $\theta_2 = \text{C7C10C9C11}$

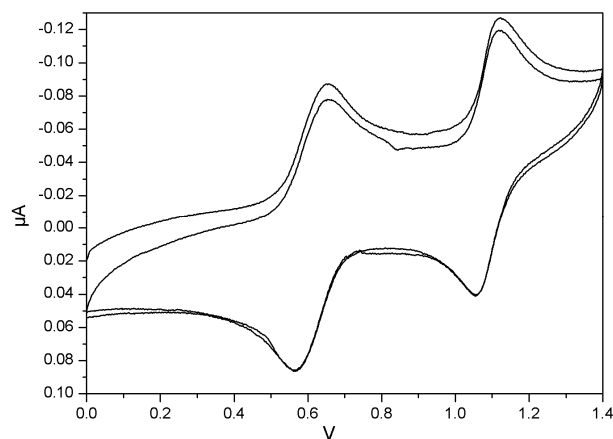
Table S10. calculated J values for (TTF-Bz-TTF)<sup>2+</sup><sub>para</sub>

	Isomer AA				Isomer AB			
	C2		Cs		C2		Cs	
	J <sub>N</sub>	J <sub>Y</sub>	J <sub>N</sub>	J <sub>Y</sub>	J <sub>N</sub>	J <sub>Y</sub>	J <sub>N</sub>	J <sub>Y</sub>
	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)	B3LYP (BP)
TZV	-9.11 (-34.50)	-9.08 (-33.33)	-11.67 (-42.29)	-11.63 (-40.60)	-10.31 (-41.27)	-10.2 (-39.89)	-11.45 (-41.62)	-11.42 (-39.99)
Aug-cc-pVDZ	-8.60 (-31.95)	-8.57 (-30.91)	-11.67 (-44.54)	-11.63 (-42.97)	-10.30 (-36.89)	-10.27 (-35.55)	-11.00 (-39.05)	-10.96 (-37.57)
IGLO-III	-8.02 (-33.23)	-8.00 (-32.33)	-11.59 (-39.81)	-11.55 (-38.28)	-10.57 (-40.10)	-10.54 (-38.83)	-10.24 (-36.60)	-10.21 (-35.29)

**Electrochemical studies.** Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of  $0.126\text{ cm}^2$  area, an  $\text{Ag}/\text{Ag}^+$  pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a  $0.1\text{ mol.L}^{-1}$  solution of  $(n\text{-Bu}_4\text{N})\text{PF}_6$  in benzonitrile. All experiments have been performed at room temperature at  $0.1\text{ V.s}^{-1}$ . Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.



**Fig. S7** Cyclic voltammetry of TTF-Bz-TTF<sub>meta</sub>.



**Fig. S8** Cyclic voltammetry of TTF-Pyr-TTF<sub>meta</sub>.